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Patent
Serial No.: 09/679,856
Attorney Docket No.: 37634-00000

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: :
Susamu TAKETOMI, et al. : Group Unit Art: 1773
Serial No. 09/679,856 : Examiner: Peter A. Nelson
Filed: October 5, 2000 :

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RESPONSE TO EXAMINER'S COMMUNICATION
REGARDING THE PETITION FOR RETROACTIVE
FOREIGN FILING LICENSE UNDER 37 C.F.R. §5.25

Applicants respectfully request the Examiner's favor in considering this short response to the Examiner's communication mailed December 6, 2002 regarding Applicants' petition for a retroactive foreign filing license under 37 C.F.R. 5.25.

The Examiner denied the petition for the retroactive foreign filing license because the declarations submitted with Applicants' petition (mailed April 13, 2001) did not contain specific information relating to the events and filings in Japan and how they relate to the present application. The Examiner's communication also notes that no declaration was submitted by Dr. Taketomi, who the co-inventors agree was responsible for the filing in Japan and has direct knowledge of the facts and circumstances surrounding that filing. Finally, the Examiner also noted that it was unclear what was the relationship between Dr. Taketomi's employer, Matsumoto Yushi-Seiyaku Ltd. and MACE, an organization that had been responsible for commercializing the technology of

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the present application to the extent that Kansas State University Research Foundation had such rights (it no longer does).

As discussed below, Applicants submit herewith the Declaration of Dr. Susamu Taketomi, which addresses all of the points raised by the Examiner. Specifically, Dr. Taketomi points out that he has been an employee of Matsumoto Yushi-Seiyaku Co. Ltd. ("Matsumoto") since August 25, 1985, and has also been a guest researcher in the United States at various institutions since 1996. Dr. Taketomi points out that the present patent application describes, among other things, four aspects of the invention:

- (a) preparation of YIG nanoparticles by an Alkoxide method,
- (b) preparation of colloidal solution of YIG nanoparticles,
- (c) after absorbing the colloidal solution in the pores of porous glass, application of a heat treatment, and
- (d) identification of the prepared materials by X-ray diffraction and electron microscopy.

Dr. Taketomi explains that while parts (a) and (b) were accomplished in Japan before 1995, parts (c) and (d) were accomplished in the United States.

Dr. Taketomi further explains that the filing in Japan (which is the only foreign filing currently in existence that corresponds to the present application) was prompted by a publication in Japan on October 6, 1999, of a newspaper article (a translation of which is provided) that described parts of the invention. Because, as Dr. Taketomi understood it, Japanese law provides that a publication can be considered prior art if an application is not made in Japan within 6 months, he directed the filing of the Japanese application (an English translation of which is provided) on April 5, 2000.

Dr. Taketomi's declaration establishes that each of the three requirements for the verified statement in 37 C.F.R. 5.25 are met:

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- (i) An averment that the subject matter in question was not under a secrecy order at the time it was filed abroad, and that it is not currently under a secrecy order;
- (ii) A showing that the license has been diligently sought after discovery of the of the proscribed foreign filing, and
- (iii) An explanation of why the material was filed abroad through error and without deceptive intent without the required license first having been obtained.

Dr. Taketomi explains that the filing in Japan without a foreign filing license was completely inadvertent and through error without deceptive intent, because he was unaware of any requirement to first obtain such a license in order to later pursue an application for patent in the United States. Dr. Taketomi further explains that the subject matter of the present application has never been under any secrecy order in Japan or the United States and was not developed in relation to any project funded, sponsored or in any way related to any government agency, including any military or nuclear power agencies of any country.

Finally, with regard to diligence, the declaration of Dr. Taketomi, together with the declarations of Drs. Sorenson and Klabunde and Mr. Trewyn filed previously, establish that no one affiliated with the present application was aware of the requirement to obtain a foreign filing license until advised by counsel in about September 2000. At that time, according to the declarations, representatives of Dr. Taketomi's employer, Matsumoto, and Mid-America Commercialization Corporation ("MACC") met to determine whether a United States application should be filed. MACC has a relationship with Kansas State University Research Foundation ("KSURF"), the former assignee of Drs. Sorenson's and Klabunde's ownership interest in the present patent application. A

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decision was taken to file, and the present application was filed on October 5, 2000. A filing receipt for the application was received on December 11, 2000.

In the period that ensued, former counsel attempted to obtain declarations from all who had personal knowledge of the facts necessary to obtain a retroactive foreign filing license. However, also at that time, Matsumoto and KSURF engaged in what would become protracted and conflicted negotiations over their respective royalty rights in the invention of the present application. Thus, while former counsel and Dr. Taketomi had exchanged drafts of a declaration in December 2000 and January 2001, former counsel was required to withdraw from representing Dr. Taketomi with respect to the filing of his declaration in January 2001 because of the conflict that had developed between the interests of Matsumoto and KSURF in the invention of the present application. For this reason, together with the fact that Dr. Taketomi left his position with Kansas State at the end of January 2001 and had no further opportunity to speak with representatives of KSURF about the matter, the original petition for a retroactive foreign filing license, filed April 13, 2001, did not include Dr. Taketomi's declaration.

By the time the PTO acted on the petition for the foreign filing license approximately 20 months later, the negotiations over rights to the invention of the present application had been resolved by the assignment of all of KSURF's rights to Matsumoto, which became the sole assignee of the present application. In January 2003, Matsumoto began evaluating its options for responding to the Examiner's communication. This included the decision to retain the undersigned as counsel of record because former counsel had traditionally represented the interests of KSURF and Matsumoto desired to retain counsel that had no previous relationship with KSURF. Once the undersigned

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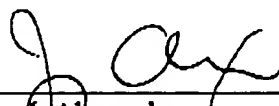
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obtained all of the files from former counsel and was able to gain a complete understanding of the factual situation, this response, together with the accompanying declaration of Dr. Taketomi, was promptly prepared and filed.

It is respectfully submitted that the facts established in Dr. Taketomi's declaration, and summarized above, establish a sufficient level of diligence under the circumstances. The diligence should be regarded as sufficient especially when considered together with the facts that: (1) the original filing in Japan was completely inadvertent and made with no deceptive intent; (2) the present invention has never been under any secrecy order in the United States or Japan and was not developed in relation to any project funded, sponsored or in any way related to any government agency, including any military or nuclear power agencies of any country; (3) the approximately six month delay between September 2000 and the filing of the petition for the retroactive license in April 2001 is reasonably explained by the facts recounted above; and (4) this six-month delay is minimal in comparison to the PTO's 20-month delay in acting on the petition.

For the foregoing reasons, Applicants respectfully request that the Examiner grant the petition for a foreign filing license and commence examination of the present application on the merits.

Respectfully submitted


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Attorney Docket No. 37634-00000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: :
Susamu TAKETOMI, et al. : Group Unit Art: 1773
Serial No. 09/679,856 : Examiner: Peter A. Nelson
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VERIFIED STATEMENT
UNDER 37 C.F.R. §5.25(a)(3)

I, SUSAMU TAKETOMI, a citizen of Japan, do declare and state that:

1. I am currently an employee of Matsumoto Yushi-Seiyaku Co. Ltd. and have been employed by them since August 25, 1985. Currently, I am also a guest researcher at the National Institute for Standards and Technology ("NIST") in Gaithersburg, Maryland. Prior to that, I was a visiting researcher at Kansas State University in the field of nanoparticle science from December 1998 until about the end of January 2001 in the laboratory of Dr. Christopher M. Sorenson. Before that, I was a visiting scholar in University of Washington from December 1996 through November 1998.
2. The origin of the present invention went back to 1990 in Japan. The present application describes, among other things, four aspects of the invention.
 - (a) preparation of YIG nanoparticles by an Alkoxide method,
 - (b) preparation of colloidal solution of YIG nanoparticles,
 - (c) after absorbing the colloidal solution in the pores of porous glass, application of a heat treatment, and
 - (d) identification of the prepared materials by X-ray diffraction and electron microscopy.

The factors (a) and (b) were accomplished in Japan before 1995. The factor (c) was accomplished when I was staying in University of Washington between 1996 through 1998. The factor (d) was accomplished when I stayed in Kansas State University between 1998 and 1999.

3. I conceived of the glass composite material that is the subject of the present patent application when I was staying in University of Washington between 1996 and 1998. I made many different samples with different heat-treatments. Unfortunately due to the lack of research funding, I could no longer research this subject in University of Washington. After arriving at Kansas State University in December 1998, I identified the samples I had previously made at the University of Washington, with the help of my co-inventors, Dr. C. M. Sorensen, Dr. K. J. Klabunde. The yttrium iron garnet (YIG) nanoparticles' amount in glass matrix was so small, that we could not identify the present sample materials with an ordinary method of X-ray diffraction and electron microscopy. Accordingly Dr. C. M. Sorensen, Dr. K. J. Klabunde and I discussed this problem and tried to overcome this difficulty. Fortunately we overcame the difficulty and successfully identified many of the sample materials of that had undergone different heat-treatments. This made clear what heat-treatment was good for the preparation of the present invention's material.
4. On October 6, 1999, a newspaper article appeared in Japan which described part of our invention. Attached Document 1 is the copy of the newspaper article and its English translation by me.
5. My understanding under Japanese law is that a patent application must be filed within six months of a publication describing the invention or else such publication will be considered prior art. Therefore, with the assistance of my employer, Matsumoto Yushi-Seiyaku Co. Ltd., I directed that a patent application for the invention, naming myself and C.M. Sorenson and K.J. Klabunde as inventors, be filed in the Japanese Patent Office. I was the person responsible for initiating and directing that filing. That application was filed in Japan on April 5, 2000 as Application No. 2000-140930. The application was later published on December 18, 2001 under Japanese law. The disclosure of the Japanese patent application is almost identical to the present application filed in the United States. Attached Document 2 is the English translation of the Japanese patent disclosure translated by me. The present application does not claim priority to the Japanese application.
6. There have been no other filings in any other country besides Japan and the United States for this invention.
7. At the time of the filing of the Japanese application, I was unaware of the need under United States law to obtain a foreign filing license and, in fact, I had not heard of such a license at that time.
8. In fact, the existence of the foreign filing license requirement seemed strange to me once I learned of it later because, as I understand it, in Japan there is no similar requirement.
9. I intended that a patent application for the invention also be filed in the United States. Therefore, in about August 2000, I presented a translation of the disclosure of the Japanese Patent Application (Document 2) to administrators at

Kansas State University in order to ascertain whether the Kansas State University Research Fund ("KSURF") would be interested in sharing in the patent royalty rights and the costs of obtaining a patent in the United States. I understand that KSURF has a relationship with the Mid-America Commercialization Corporation ("MACC") which assists KSURF to commercialize inventions in which KSURF has an interest.

10. Ultimately, KSURF agreed to assist in the preparation and filing of the present application. A patent attorney, Mr. Collins, recommended by KSURF prepared and filed the present application in the United States as Serial No. 09/679,856 on October 5, 2000.
11. In about December 2000, I was informed by Mr. Collins' firm of the need to submit an affidavit to obtain a retroactive foreign filing license. In December 2000 and January 2001, we exchanged drafts of an affidavit but I was unsatisfied with the draft affidavit prepared by Mr. Collins' firm. During this time period, because the relative contributions of my self and Drs. Sorenson and Klabunde were not equal, Matsumoto and KSURF became involved in what would become protracted and conflicted negotiations over the relative share of patent royalty rights that each organization should own in the invention.
12. On January 26, 2001, I received a letter from Mr. Collins stating that: "It appears that a dispute has arisen between you (and perhaps your employer) and KSURF." The letter continued that because Mr. Collins' lawfirm has traditionally represented KSURF, that Mr. Collins could no longer represent me in the matter.
13. Also, on or about January 31, 2001, I left my position at KSURF to move to my present position at NIST. Thus, I had no chance to speak with KSURF's staff directly about this issue. I later learned that, some time after I left Kansas State, affidavits of others who were not directly involved in the making of the invention, were filed in support of a request for a retroactive foreign filing license.
14. While the issue of the foreign filing license was pending in the USPTO, the negotiations over the patent rights were finally resolved. In about September 2002, KSURF agreed that it would assign all of its ownership rights in the present application (which KSURF had received by assignment from Drs. Sorenson and Klabunde) to Matsumoto Yushi-Seiyaku Co. Ltd.
15. I was informed in December 2002 that the USPTO had denied the petition to grant a retroactive foreign filing license primarily because it lacked information from those knowledgeable about the patent filing in Japan, and inviting the submission of further information.
16. During January 2003, myself and my employer, Matsumoto Yushi-Seiyaku Co. Ltd., evaluated the decision of the patent examiner and decided what we should do in response. Mr. Collins' firm traditionally represented the interests of KSURF and had written the letter in January 2001 stating that he was withdrawing from representing my interests and that of my employer. We believed it was important to seek a different lawfirm that would clearly represent

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the interests of Matsumoto Yushi-Seiyaku Co. Ltd. and myself, with no prior conflict.

17. In February 2003, I visited the law office of Mr. Jay Alexander (who was recommended to me by another lawyer) and asked if he would be willing to represent Matsumoto Yushi-Seiyaku Co. Ltd. and myself in this matter. An agreement for the representation was reached at the end of March 2003.
18. Mr. Alexander then began to review the materials that I had provided from my files and to make arrangements with Mr. Collins' firm to obtain a transfer of their files. Because I am primarily a Japanese speaker and not an English speaker, it was necessary for Mr. Alexander to make a detailed review of the written materials to gain a complete understanding of the factual situation in order to be able to assist me in preparing this affidavit in response to the examiner's request for further information.
19. It is important to point out that the failure to initially obtain a foreign filing license for this invention was completely inadvertent. As I stated above, I directed the filing in Japan in order to avoid the prior art effect of the October 6, 1999 article and was completely unaware at that time that if an application for this invention were to be filed in the United States in the future, that a foreign filing license must be obtained.
20. Finally, it is also important to note that the subject matter of the present application has never been under any secrecy order in Japan or the United States and was not developed in relation to any project funded, sponsored or in any way related to any government agency, including any military or nuclear power agencies of any country.

Dated: May 27, 2003

Signed: Susamu Taketomi
SUSAMU TAKETOMI

Document 1

Nikkan Kougyou Newspaper (Daily Industrial Newspaper) (Japan) October 6, 1999

Matsumoto Yushi-Seiyaku Co. Ltd. and Kansas State University in USA developed Magneto-optical recording media

The recording density increased 500 times as large as the conventional ones. YIG particles were inserted in the pores of glass.

The cooperating research group of Matsumoto Yushi-Seiyaku Co. Ltd. and Kansas State University succeeded in developing new-type magneto-optical recording media the recording density of which is 500 times as large as the conventional ones. They made the material by dispersing ultrafine particles of ferrimagnetic material, yttrium-iron-garnet (YIG), in the nanometer-size pores of special glass called thirsty glass.

For conventional magnetic recording method, the information is recorded in the magnetic recording media by dividing its surface into many different magnetic area. On the contrary, for the present new method of using magneto-optical media, individual YIG particle which is embedded in glass as a minimum recording unit instead of the magnetically divided surface area. Accordingly the recording density of the present media increases as large as 1 Gbits per square mm compared with 2 Mbit per square mm for the conventional magnetic hard disk. The present new media was developed by cooperating research group, Prof. C. Sorensen of Physics and Prof. K. Klabunde of Chemistry in Kansas State University in USA and Dr. S. Taketomi of Matsumoto Yushi-Seiyaku Co. Ltd.. Dr. Taketomi has already succeeded in preparing YIG nanoparticles by special chemical method, alkoxide method. They expected that using the thirsty glass which was synthesized in USA, if they introduced the YIG nanoparticles into the pores of this glass, they could obtain a high density magneto-optical recording media. So they started the research. First dispersing YIG nanoparticles, which were prepared by the alkoxide method, in the solvent, they made colloidal solution. Then they introduced the colloidal solution into the pores of the thirsty glass. After heat treatment, the pores were melted and the colloidal particles of YIG were left in the glass. The number density of the pores of the thirsty glass amounts to 1 billion per square mm. Accordingly the high density recording media of 1Gbit per square mm can be theoretically obtained. The read and write recording method is as follows. The information is written in the media by altering the magnetization direction of the YIG particle by laser heating and the written information is read by optical method. The present media has several disadvantages such as the particles size is distributed and particles dispersion is not uniform. But Dr. Taketomi said that these technical problems can be overcome by technical improvement in the future. Figure caption: YIG nanoparticles embedded in the thirsty glass

Document 2

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Title

Rare earth iron garnet nanoparticles-dispersed glass composite

Inventors

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Christopher M. Sorensen 3925 Snowy Reach, Manhattan, KS 66503
Kenneth J. Klabunde 105 Notre Dame Circle, Manhattan, KS 66503

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Body

Title

Rare earth iron garnet nanoparticles-dispersed glass composite

Claim

Claim 1 After introducing amorphous rare earth iron garnet nanoparticles into nanometer-size pores of porous glass, the particles are transformed to crystallized rare earth iron garnet nanocrystals by heat treatment. At the same time, the porous glass is transformed to ordinary glass by fusing the pores by the heat treatment. Finally the glass composite dispersed with the rare earth iron garnet nanocrystals of high number density is synthesized.

Claim 2 In Claim 1, the size of the pore dimension of the porous glass is between 15 and 400 nm.

Claim 3 In Claim 1, the amorphous rare earth iron garnet nanoparticles are prepared by alkoxide method.

Claim 4 In Claim 1, a colloidal solution of the amorphous rare earth iron garnet nanoparticles as colloidal particles is made and then the colloidal solution is absorbed into the pores of the porous glass to introduce the amorphous rare earth iron garnet nanoparticles into the pores of the porous glass.

Claim 5 In Claim 1, the heat treatment is carried at temperatures between 650°C and 850°C for about 2 hours in air or nitrogen gas or an inactive gas environment.

Claim 6 In Claim 1, the heat treatment is carried as follows; the material is heated at the rate of 100°C/hour or faster and when the temperature reaches as high as about 900°C, the material is cooled rapidly to the room temperature.

Claim 7 ~~In Claim 1,~~ (the rare earth iron garnet nanocrystals are dispersed in the surface glass composite in which)

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layer of the glass with number density between 10^7 and 10^9 particles/mm² with respect to surface.

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Detailed description of the present invention

1. Technological fields to which the present invention belongs

The present invention is related to the glass composite which contains magnetic nanoparticles in high density.

2. Conventional technology

We have already successfully prepared the amorphous yttrium-iron-garnet (YIG) nanoparticles by an alkoxide method^{1,2}. The preparation of the magnetic nanoparticles-dispersed composite is very important because it is a high density magnetic information storage material. In addition, the reduction of the size to nanometer scale may enhance the novel properties which the same bulk material does not possess, the quantum size effect^{3,4}. The magnetic fine particles, however, tend to spontaneously coagulate by mutual magnetic attraction due to their magnetic dipole moment, and their intrinsic magnetic characteristics are often smeared by the coagulation even though very fine magnetic particles were successfully prepared. There have been methods developed to prevent the coagulation of magnetic fine particles, such as dispersion of the magnetic fine particles in an organic binder (magnetic pigment or magnetic tape).

3. Problems which the present invention overcomes

The previous method uses mechanical stirring to disperse the particles, and a considerable portion of the particles still remain coagulated. The mechanical fragility of the dispersed composite occurs.

We succeeded in preparing a high density rare earth iron garnet nanocrystal-dispersed glass composite; first we introduce the amorphous rare earth iron garnet nanoparticles into the pores of the porous glass, then by heat treatment we crystallized the particles to rare

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earth iron-garnet nanocrystals and at the same time let the pores of the glass fuse, and finally we obtain the rare earth iron garnet nanocrystal-dispersed region with high number density in the surface layer of the glass.

Here the term "nano particle" is defined as a particle, the size of which is between a several nanometers and several hundred nanometers, the term "nanocrystal" is defined as a crystal grain the size of which is between a several nanometers and several hundred nanometers. We confine the term "rare earth iron garnet" to the following chemical formula, $\text{Fe}_3\text{Y}_{3-x-y}\text{M}_x\text{N}_y\text{O}_{12}$ with the garnet crystal structure. Here M and N denote either Y, Bi, Gd, In or rare earth elements La, Ce, Pr, Nd, Pm, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, and Ln. x and y denote the numbers satisfying $0 \leq x + y \leq 1$.

4. Solution

The merit of the present invention, the preparation of the rare earth iron garnet nanocrystal-dispersed glass composite, consists of the following procedure. The amorphous rare earth iron garnet nanoparticles which are nonmagnetic are introduced into the nano-size pores of the porous glass. After heat treatment, the amorphous rare earth iron garnet nanoparticles are crystalized to the rare earth iron garnet nanocrystals which are ferrimagnetic. At the same time the glass pores fuse and thereby entrap the nanocrystals due to the heat treatment and the rare earth iron garnet nanocrystal-dispersed glass composite is finally obtained.

The advantages of the present invention are:

1. As the dispersed nanocrystals, the rare earth iron garnet nanocrystals, show strong magneto-optical effect, the rare earth iron garnet nanocrystal-dispersed glass composite is suitable for magneto-optical devices.
2. As the particles are dispersed in the glass as nanocrystals, they might show quantum size effect, i.e., they might show stronger magneto-optical effect compared with the bulk rare earth iron garnet.

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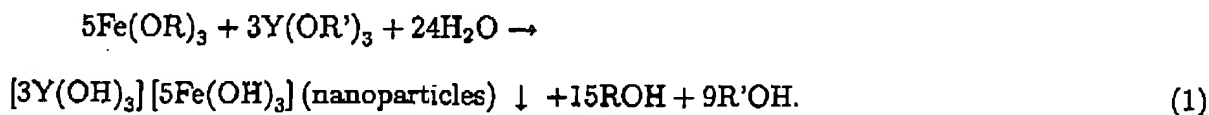
3. As the particles are dispersed in the surface layer of the glass with high number density in a unit area, the composite is suitable for a media of high density magneto-optical memory storage.
4. It is easy to disperse the precursor particles in the pores of the glass without coagulation because magnetic nanocrystal precursors are nonmagnetic.
5. The glass composite is suitable for the magneto-optical devices because the glass matrix is transparent to visible light.

5. Preparation methods in detail

A. Preparation of $\text{Fe}_5\text{Y}_{3-x}\text{M}_x\text{O}_{12}$ nanoparticles by the Alkoxide method

In the following we show the concrete method of preparing the amorphous $\text{Fe}_5\text{Y}_3\text{O}_{12}$ nanoparticles as an example.

Starting materials are solutions of Fe^{3+} alkoxide $\text{Fe}(\text{OR})_3$ and solution of yttrium alkoxide $\text{Y}(\text{OR}')_3$, where R and R' denote alkyl groups such as ethyl and butyl groups. The two solutions are mixed so that the molar ratio of Fe over Y should be 5 : 3 stoichiometrically. By adding water to these mixture solutions, hydrolysis occurs to produce nanoparticles of the mixture of amorphous iron oxide and yttrium oxide expressed by

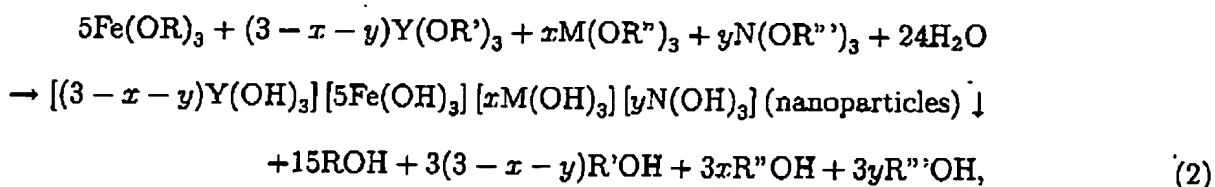


In this hydrolysis, if ordinary water liquid is added to the solution, nanoparticles are not synthesized but much larger particles are prepared. If one wants to prepare nanoparticles, one has to heat the mixture solution of the iron alkoxide and the yttrium alkoxide in the boiling state with strong stirring. One has to introduce hot water vapor of 100°C into this boiling mixture solution and let the hydrolysis be made¹. Then one can obtain nanoparticles

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of less than 10 nm in diameter. These nanoparticles are a mixture of the iron and yttrium oxides with an amorphous state the molar ratio of Fe over Y is 5 : 3.

If one wants to prepare nanoparticles of the chemical formula, $\text{Fe}_5\text{Y}_{3-x}\text{M}_x\text{O}_{12}$, or $\text{Fe}_5\text{Y}_{3-x-y}\text{M}_x\text{N}_y\text{O}_{12}$, the following chemical reaction is used,



where, M and N denote either Bi, Gd, In or rare earth elements La, Ce, Pr, Nd, Pm, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, and Ln. x and y denote the numbers satisfying $0 \leq x + y \leq 1$, R'' and R''' denote alkyl groups.

These nanoparticles, or the primary particles, coagulate with each other and make aggregates, or the secondary particles. By centrifuge, one obtains these secondary particles as deposits in the solution. These secondary particles are too large to introduce into the nanometer-size pores of the porous glass. We took the following procedure to make the colloidal solution dispersing the primary particles as the colloidal particles and introduce the solution containing the primary particles into the nanometer-size pores of the porous glass.

B. Preparation of the colloidal solution with the aid of surfactant

One has to decompose the secondary particles into the primary particles (nanoparticles) and disperse these primary particles in water or organic solvent. Therefore we put the deposit or the secondary particles obtained by the centrifuge into a solvent such as kerosene together with a suitable surfactant such as oleic acid, and milled the secondary particles into the primary particles by high speed ball mill or roll mill or jet mill or sand mill. During this process, the secondary particles are broken into the primary particles and their surface is coated with the surfactant molecules. Accordingly the primary particles, or nanoparticles,

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are stably dispersed in the solvent. Sometimes the surface of the particles is not completely covered with the surfactant molecules and the dispersing stability is not fully obtained. In such a case the following additional procedure is taken.

After ball milling, oleic acid and aqueous ammonia are added to the solution. This creates ammonium oleate in the solution. Stirring this solution strongly with a homogenizer, it is heated as high as 98°C. The ammonium oleate decomposes to ammonia gas and oleic acid above 78°C, and the isolated oleic acid molecules adhere to the surface of the nanoparticles and cover their surface. Accordingly the particles are stably dispersed in the solvent. On the other hand, the primary particles are distributed widely in size. During this process, the large particles deposit in the bottom of the solution. Finally we obtain the supernatant of the solution which contains only the particles as small as 30 nm or smaller. After this procedure, the solution was separated into two phases, the water solvent layer and oil solvent layer. We decantate the oil-solvent phase. The particle fraction of this solution is so small that we condense the solution by an evaporator.

C. Introduction of amorphous rare earth iron garnet nanoparticles into pores of porous glass

1. Porous glass possessing pores of nanometer dimension

Porous glass possessing nanometer-size pores is generally called thirsty glass and is mainly classified into two groups. The former group is so-called vycore glass which are produced by Dow Corning Co. The other group is called controlled pore glass (CPG) which were prepared by W. Haller⁵.

The former is prepared as follows. First a ternary oxide melt ($\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$) is rapidly cooled and it solidifies into two different phases. This phase separation is spinodal decomposition and accordingly the precipitated phases, $\text{Na}_2\text{O-B}_2\text{O}_3$ and SiO_2 phases intrude each other with nanoscale dimension. After removing the former phase by acid, the latter

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phase or SiO_2 phase remains. Finally the porous SiO_2 glass with nanometer-size pore is prepared.

The latter is prepared as follows. First a ternary oxide melt ($\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$) is rapidly cooled and it solidifies into a homogeneous glass. After reheating and annealing at elevated temperature, it segregates into two interconnected phases. One of them is almost pure silica and the other is sodium borate with some silica dissolved. After removing the sodium borate phase by acid and cleaning silica debris from the pores, CPG is prepared. The pore size of the CPG is more uniform than those of vycor glass. Figure 1 is scanning electron microscope (SEM) photograph of the carbon replica from the CPG surface. The pores of honeycomb structure are observed.

In our basic experiment, we used vycor glass plate of 2.5 cm square with pore size of 11 nm in average diameter. We also used four different CPG with pore size of 48.6, 114, 204 and 292 nm in average diameter. The CPG which was used in our experiment was powder of about $50\mu\text{m}$ in dimension.

2. Introduction of rare earth iron garnet nanoparticles to pores of porous glass

Soaking the vycor glass plate in the colloidal solution of the rare earth iron garnet nanoparticles, we tried to introduce the rare earth iron garnet nanoparticles into the pores of the vycor glass. The real rare earth iron garnet nanoparticles which we used in our experiment were yttrium iron garnet (YIG) nanoparticles, ($\text{Fe}_3\text{Y}_3\text{O}_{12}$). About one day after the vycor plate was soaked in the colloidal solution, we took the plate out of the solution and dried it in the air. Accordingly the solvent in the pores of the glass was evaporated. In reality, this experiment failed because no particles went into the pores. It is due to the pore size of 11 nm, i.e., the pore size is too small to introduce the particles into the pore.

When we used CPG powder in our experiment, we put the CPG in a vial, then we poured the colloidal solution in the vial. Accordingly the pores of the glass absorbed the solution. After filtering the CPG glass with the absorbed solution and removed the excess solution,

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the CPG glass was dried in the air and the solvent in the pores was evaporated. Figure 2 (a) is the schematic figure of the CPG with the amorphous YIG nanoparticles left in the pores.

D. Crystallization of the YIG colloidal particles and the porous glass fusion; Heat treatment condition

1. Heat treatment

After heat treatment, the pores were fused and at the same time the amorphous YIG particles were crystallized and embedded in the glass. See Fig. 2 (b). Nanocrystals of different compounds other than YIG were prepared by an improper heat treatment. The following experiments were made to find out the suitable heat treatment condition to obtain the rare earth iron garnet nanocrystals. We examined YIG nanocrystals as the rare earth iron garnet. The suitable heat treatment condition for other rare earth iron garnet nanoparticles-dispersed glass composite can be estimated from that of YIG.

An electric furnace was used for calcination of the samples. The temperature was increased at the rate of 200deg/hour from room temperature as high as T_0 and the temperature was held for t_0 hours (Table 1). Then the samples were cooled to room temperature. We made many samples of different heat treatment conditions. The characteristics of the samples are tabulated in Table 1. They were calcined in air except samples B₃ and D which were calcined in a N₂ gas environment.

2. Identification of prepared materials by X-ray diffraction

Figure 3 shows the XRD patterns from the samples after calcination at the temperatures from 700°C to 1000°C. The pore size of CPG before calcination was 292nm and the calcination time, t_0 , was 2 hours for all the samples. The XRD curves in this paper are all shown without smoothing treatment. It shows that YIG and cristobalite were independently pre-

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pared for the sample calcined at temperature less than 800°C. The peaks marked with ○, ●, ⊙, ..., denote individual compounds which are shown in Fig. 3's figure caption. These marks are common in Figs. 4, 5, and 6. A YIG crystal was prepared for the sample of the calcination temperature, $T_0 = 700^\circ\text{C}$. The mean crystalline size, D , of the YIG nanoparticles was estimated by the half value width, Δ , of the (420) peak ($2\theta = 32.314^\circ$) of YIG and the half value width, Δ_{st} of the (112) peak ($2\theta = 50.138^\circ$) of standard multicrystalline quartz, using expression,

$$D = \frac{0.9\lambda}{(\Delta - \Delta_{st}) \cos \theta}, \quad (3)$$

where $\lambda = 1.54 \text{ \AA}$ is the X-ray wavelength and 2θ is the diffraction angle. The D value for each sample is shown in Table 1. YIG's D increases rapidly with the calcination temperature. Many iron silicate and yttrium silicate compounds were prepared by the reaction of YIG particles and CPG or silicate for the samples of T_0 above 850°C. The identified products are tabulated in Table 1. In addition, there are a few peaks which cannot be identified. There are several polymorphisms for the same chemical formula of iron silicate and yttrium silicate. Therefore it may be that several kinds of polymorphism of iron silicate and yttrium silicate were prepared in the contact region between YIG particles and CPG.

Figure 4 shows the XRD patterns of the samples of T_0 at 700°C and up to 1200°C with small CPG pores. The calcination time, t_0 was 2 hours and the mean pore diameter before calcination was 48.6 nm for all the samples. All the samples were calcined in the air except sample B₃ which was calcined in a N₂ gas environment. The YIG particles were decomposed to different compounds for the samples of $T_0 \geq 800^\circ\text{C}$. In addition, the iron and yttrium silicate disappeared and YIG particles decomposed almost to $\alpha\text{-Fe}_2\text{O}_3$ and Y_2O_3 for the sample of $T_0 = 1200^\circ\text{C}$.

Figure 5 shows XRD patterns of the samples for different calcination time, t_0 from 0 hour to 16 hours. T_0 was not the same for these samples. The meaning of $T_0 = 890, t_0 = 0$ for sample A₉ is as follows. The furnace temperature was increased as high as 890°C at the rate of 200 deg/hour. The moment the temperature reached $T_0 = 890^\circ\text{C}$, the power of the

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furnace was turned off and the sample temperature was decreased spontaneously. From the result of sample A₆, it was revealed that YIG particles and silicate reacted to form iron and yttrium silicate during long time heat treatment even at a low temperature calcination of 675°C. This fact indicates that iron or yttrium silicates are more stable than the separated state of YIG and silica.

Figure 6 shows the XRD results for the samples of pore size 204 nm and 114 nm before calcination. Sample D was calcined in a N₂ gas environment.

3. *Transmission Electron Microscopy*

In this section we show that the YIG nanocrystals were dispersed in the glass in the prepared samples by electron microscopy.

The calcined samples were ground with an agate mortar to reduce the grain size from about 50 μ m to submicron in dimension to allow transmission of the electron beam. The milling powder was mostly pure silica without YIG particles because the amorphous YIG particles in the original CPG grains were concentrated only in 0.5 μ m subsurface layer. Significant color changes were observed after removing this subsurface layer. For example, sample B₄ was tinged with deep red color due to α -Fe₂O₃ which was formed by decomposition of YIG particles during calcination. After grinding, the color changed to white pink because of white cristobalite in the core of CPG grains revealed by grinding. The ground powder was put in a vial filled with 97 % ethanol and stirred strongly. Before all the fragments deposited in the bottom of the vial, the supernatant liquid was removed so that excess pure silica fragments were removed. In fact, the specific gravity of CPG fragments which contained YIG nanocrystals was greater than that of pure CPG fragments. In addition, the former fragments were easy to coagulate due to the YIG magnetic attraction. Accordingly, the CPG fragments with YIG nanocrystals deposited faster than the pure CPG fragments. Taking advantage of this nature, we separated the CPG fragments. This process was done several times. Lastly as soon as the liquid was stirred strongly, a droplet of the

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liquid was put on polymer film of a copper mesh and the CPG fragments were observed by two transmission electron microscopes (TEM).

Figures 7, 8, and 9 are the TEM photographs of sample A₁, A₂ and A₃, respectively. The small black dots in the silica matrix are the crystalline YIG particles or iron yttrium silicate nanocrystals. These figures identify that the nanocrystals are really distributed in the glass matrix. If we choose suitable conditions, we can distribute the nanoparticles in the surface layer of the glass with the particle concentration of 10⁹ particles/mm².

4. Heat treatment conditions

The experiment showed that the heat treatment to prepare only YIG nanocrystals in the glass is confined to very severe limits.

From the above experimental results the following speculations are possible. Three different processes occurred in parallel in the present calcination. Figure 10 contains schematic figures to explain these processes. Figure 10(a) is the state before the calcination. Both the particles and the CPG were in an amorphous phase. The radius of the circles which denote oxygen, iron, yttrium and silicon ions, respectively, are proportional to each ion's radius. The first process is the phase transition of YIG particles from amorphous to crystalline state. The second process is the phase transition of CPG from amorphous to cristobalite crystal. These two processes were shown in Fig. 10(b). The third process is the reaction of YIG particles and the contacting CPG to prepare iron silicate and yttrium silicate, which is schematically shown in Fig. 10(c). The third process proceeds slowly compared with the first and second processes in the low temperature calcination. Accordingly it seems that only the first and second processes proceed in the low temperature calcination for short calcination time. The CPG of small pores has large surface area contacting the YIG particles, and accordingly the third process proceeds notably even in low temperature short time calcination. In addition, in the calcination of high temperature as high as 1200°C, the yttrium and iron silicate transformed to more stable compounds, α -Fe₂O₃, Y₂O₃, and SiO₂. (See

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Fig. 10(d))

In conclusion, for the purpose of preparing YIG nanocrystals dispersed in silica glass, the calcination should be carried out by increasing the temperature as rapidly as possible and immediately after the temperature reaches a temperature near 900°C, at which the amorphous YIG particles are crystallized, the temperature should be decreased lest the reaction between YIG and silica should occur.

Application fields; high density magnetooptical information storage material

6. Basic principle

The conventional magnetic information storage media consists of glass or polymer substrate and magnetic alloy thin film which is coated or deposited on the substrate. One bit memory region in such a memory medium occupies one magnetic domain region which is as large as $1\mu\text{m}^2$. Accordingly there is a upper limit in making the high density information storage if one uses the conventional structure of the magnetic information storage media. Several attempts have been done to overcome this limitation. For example, after making nanosize array pattern on the nonmagnetic substrate surface by photomasking, magnetic metal thin film is deposited on this surface by sputtering or ion plating. Finally after removing the photomasking pattern, one obtains magnetic nanoparticles on the substrate surface. In this case the magnetic particle's size and interval is about 100 nm, and high density magnetic information storage media is obtained.

7. Advantage of rare earth iron garnet nanocrystal-dispersed glass composite

The above high density magnetic information storage medium has a fatal disadvantage. As sputtering or ion plating are used for fabrication, one cannot make nanometer size particle

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array of the compound of complex crystal structure such as the rare earth iron garnet due to the difficulty in keeping strictly the stoichiometric ratio. The present rare earth iron garnet nanocrystal-dispersed glass composite is suitable for such a high density magneto-optical information storage media. As one bit memory is assigned to an individual nanocrystal, anomalous increase in memory density is possible for the present material. For example, if YIG nanocrystals of 20 nm in diameter are dispersed in the glass with a 30 nm interval, 10^9 particles exist in 1 mm^2 surface of this material and the memory density of 1 Gbit/mm^2 is obtainable. The recording density of the present hard disk is 2 Mbit/mm^2 . Therefore a high density medium 500 times denser than the conventional one will be obtainable.

Effect of the present invention

After introducing amorphous rare earth iron garnet nanoparticles into nanometer-size pores of porous glass, we succeeded in crystallizing the particles to nanocrystals dispersed densely in the glass surface layer. This rare earth iron garnet nanocrystal-dispersed glass composite is most suitable for the high density magneto-optical information storage media; one nanocrystal keeps one bit memory and a great increase in memory density is obtainable.

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FIGURES

Fig. 1. Carbon replica scanning electron micrograph of CPG surface

Fig. 2. Schematic figure of CPG with YIG nano particles

Though Fig. 2(a) is a spherical grain showing the pores in the periphery and center areas, the real CPG grains are irregularly shaped and the pores exist in all the regions of the grain.

Fig. 3. Calcination temperature, T_0 , dependence of XRD patterns for samples of large pore CPG

The calcination time, $t_0 = 2$ hours, for all samples, the pore size of CPG before calcination was 292 nm for all samples. The figures in parentheses are the calcination temperature ($^{\circ}\text{C}$) and time (hour), respectively.

Peak marks are as follows and they are used in common in Figs. 8, 9 and 10. \bullet : $\text{Fe}_5\text{Y}_3\text{O}_{12}$, \bigcirc : cristobalite(1), \odot : cristobalite(2), \otimes : quartz, \triangle : $\text{Y}_2\text{Si}_2\text{O}_7(1)$, \blacktriangle : $\text{Y}_2\text{Si}_2\text{O}_7(2)$, ∇ : $\text{Fe}_2\text{SiO}_4(1)$, \blacktriangledown : $\text{Fe}_2\text{SiO}_4(2)$, \times : Y_2SiO_5 , \diamond : $\alpha\text{-Fe}_2\text{O}_3$, \blacklozenge : $\epsilon\text{-Fe}_2\text{O}_3$, \square : Y_2O_3 .

Fig. 4. Calcination temperature, T_0 , dependence of XRD patterns for samples of small pore CPG

The calcination time, $t_0 = 2$ hours, for all samples, the pore size of CPG was 48.6 nm for all samples. The figures in parentheses are the calcination temperature ($^{\circ}\text{C}$) and time (hour), respectively. Peak marks are listed in the caption of Fig. 3.

Fig. 5. Calcination time, t_0 , dependence of XRD patterns

The pore size of CPG was 292 nm for all samples. The figures in parentheses are the calcination temperature ($^{\circ}\text{C}$) and time (hours), respectively. Peak marks are listed in the caption of Fig. 3.

Fig. 6. XRD patterns of samples with CPG pores, 114 and 204 nm

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The figures in parentheses are the calcination temperature (°C) and time (hours), respectively. Peak marks are listed in the caption of Fig. 3.

Fig. 7. TEM photograph of sample A₁

Fig. 8. TEM photograph of sample A₂

Fig. 9. TEM photograph of sample A₃

Fig. 10. Schematic figure of heat treatment process of YIG amorphous particles and CPG

TABLES

Table 1. Characteristics of samples

T_0 : calcination temperature ($^{\circ}\text{C}$), t_0 : calcination time (hour), D : YIG nanocrystal's mean diameter (nm). sample A_i , ($i = 1 \sim 9$): CPG pore size before calcination 292nm, sample B_i , ($i = 1 \sim 4$): CPG pore size before calcination 48.6nm, sample C: CPG pore size before calcination 204nm, sample D: CPG pore size before calcination 114nm. The compounds were identified according to the Powder Data File of Joint Committee on Powder Diffraction Standard (JCPDS). The compounds correspond to the JCPDS number, respectively.

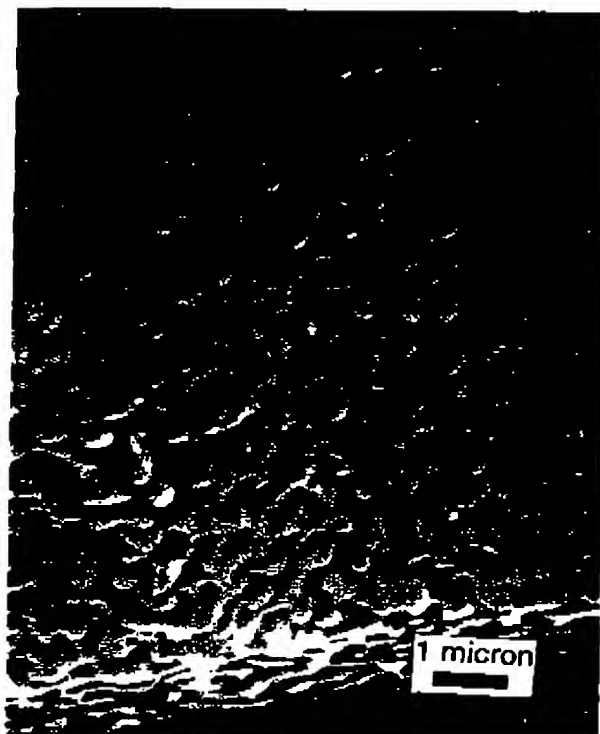
cristobalite(1):39-1425, cristobalite(2):76-0936, quartz:83-2465, $\text{Fe}_5\text{Y}_3\text{O}_{12}$:43-0507, $\text{Y}_2\text{Si}_2\text{O}_7$ (1):45-0042, $\text{Y}_2\text{Si}_2\text{O}_7$ (2):21-1459, Fe_2SiO_4 (1):71-1667, Fe_2SiO_4 (2):72-0297, Y_2SiO_5 :21-1461, $\alpha\text{-Fe}_2\text{O}_3$:80-2377, $\epsilon\text{-Fe}_2\text{O}_3$:16-0653, Y_2O_3 :44-0399

Samp.	T_0	t_0	Prepared compounds identified from XRD	D
A_1	700	2	cristobalite(1), $\text{Fe}_5\text{Y}_3\text{O}_{12}$	4.2
A_2	800	2	cristobalite(1), $\text{Fe}_5\text{Y}_3\text{O}_{12}$	37
A_3	850	2	cristobalite(1), $\text{Fe}_5\text{Y}_3\text{O}_{12}$, $\text{Y}_2\text{Si}_2\text{O}_7$ (1), Fe_2SiO_4 (1), Y_2SiO_5	unknown
A_4	900	2	cristobalite(1), $\alpha\text{-Fe}_2\text{O}_3$, $\text{Y}_2\text{Si}_2\text{O}_7$ (1), $\text{Y}_2\text{Si}_2\text{O}_7$ (2), Fe_2SiO_4 (2), Y_2SiO_5	none
A_5	1000	2	cristobalite(1), $\alpha\text{-Fe}_2\text{O}_3$, $\text{Y}_2\text{Si}_2\text{O}_7$ (1), $\text{Y}_2\text{Si}_2\text{O}_7$ (2), Fe_2SiO_4 (2), Y_2SiO_5	none
A_6	675	16	cristobalite(1), $\text{Fe}_5\text{Y}_3\text{O}_{12}$, $\text{Y}_2\text{Si}_2\text{O}_7$ (1)	11.2
A_7	700	16	cristobalite(1), $\text{Fe}_5\text{Y}_3\text{O}_{12}$, Y_2SiO_5 (1)	22.0
A_8	793	0.1	cristobalite(1), $\text{Fe}_5\text{Y}_3\text{O}_{12}$, $\text{Y}_2\text{Si}_2\text{O}_7$ (1)	37.0
A_9	890	0	quartz, $\text{Fe}_5\text{Y}_3\text{O}_{12}$	41.0
B_1	700	2	cristobalite(2), $\text{Fe}_5\text{Y}_3\text{O}_{12}$, Y_2SiO_5	unknown
B_2	800	2	cristobalite(1), $\epsilon\text{-Fe}_2\text{O}_3$, Y_2O_3	none

2C
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B ₃	900	2	cristobalite(1), Y ₂ Si ₂ O ₇ (1), Y ₂ Si ₂ O ₇ (2), Y ₂ SiO ₅ , Fe ₂ SiO ₄ (1)	none
B ₄	1200	2	cristobalite(2), α-Fe ₂ O ₃ , Y ₂ O ₃	none
C	800	2	cristobalite(1), Fe ₅ Y ₃ O ₁₂	unknown
D	900	2	cristobalite(1), ε-Fe ₂ O ₃ , Y ₂ Si ₂ O ₇ (1), Y ₂ Si ₂ O ₇ (2)	none

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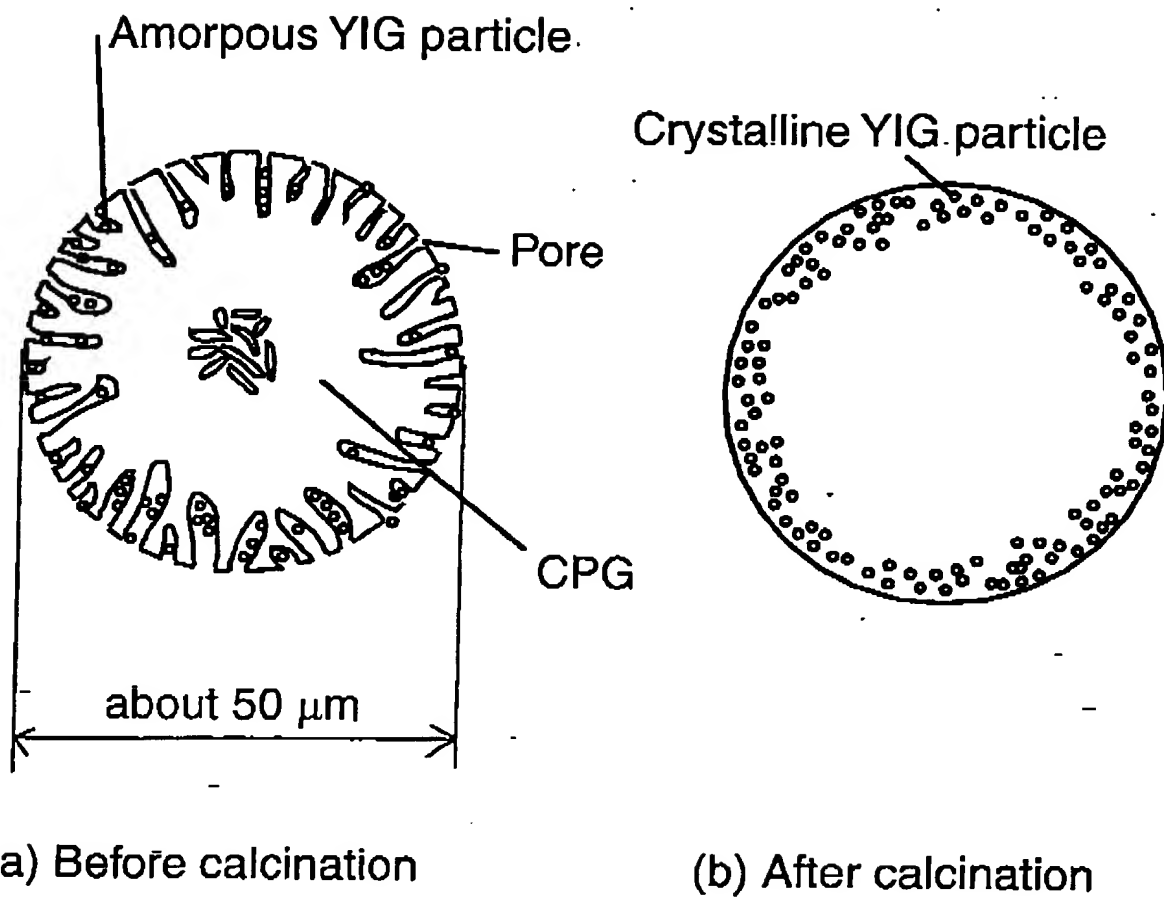
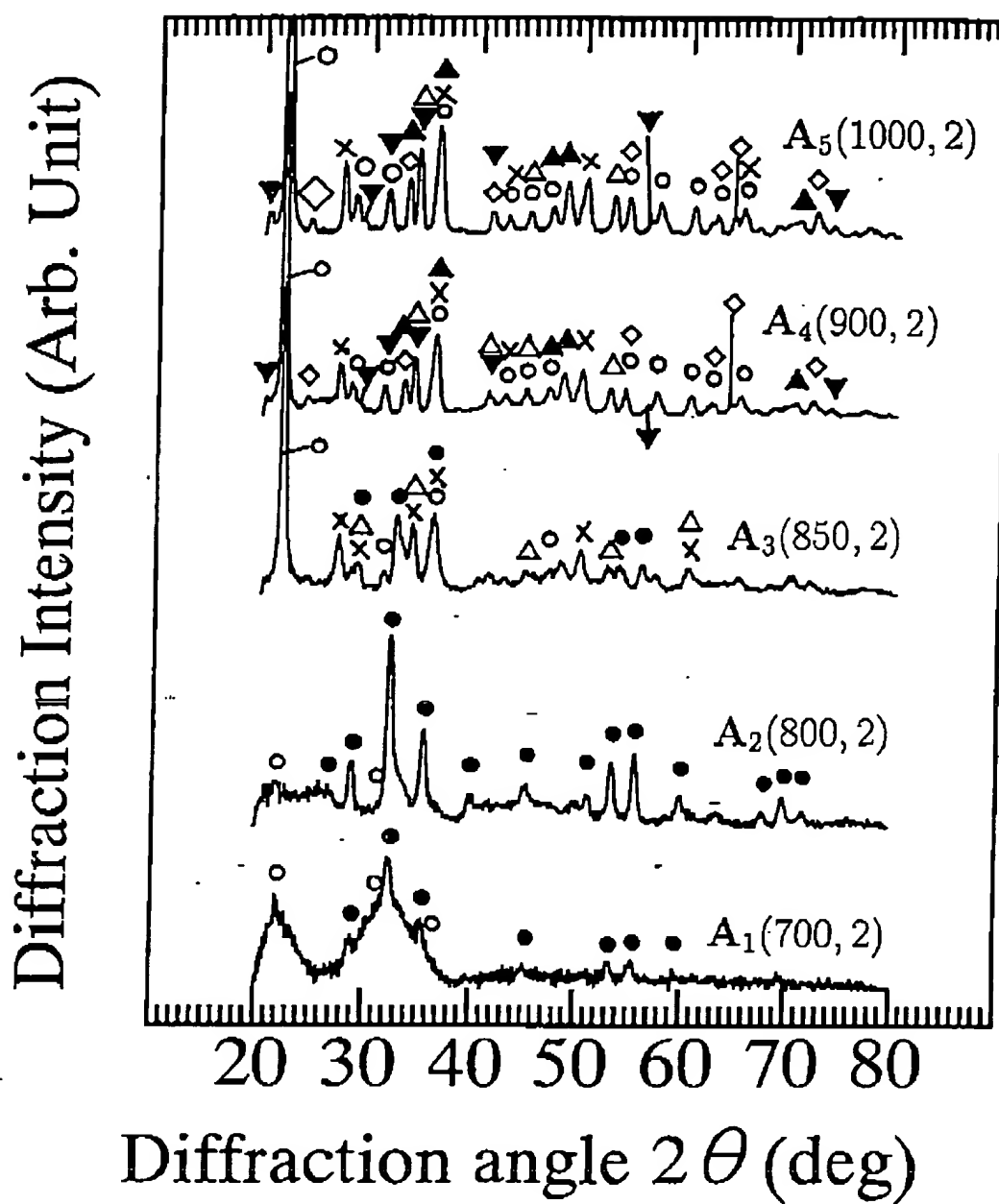


Fig. 2

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F. 1. 3

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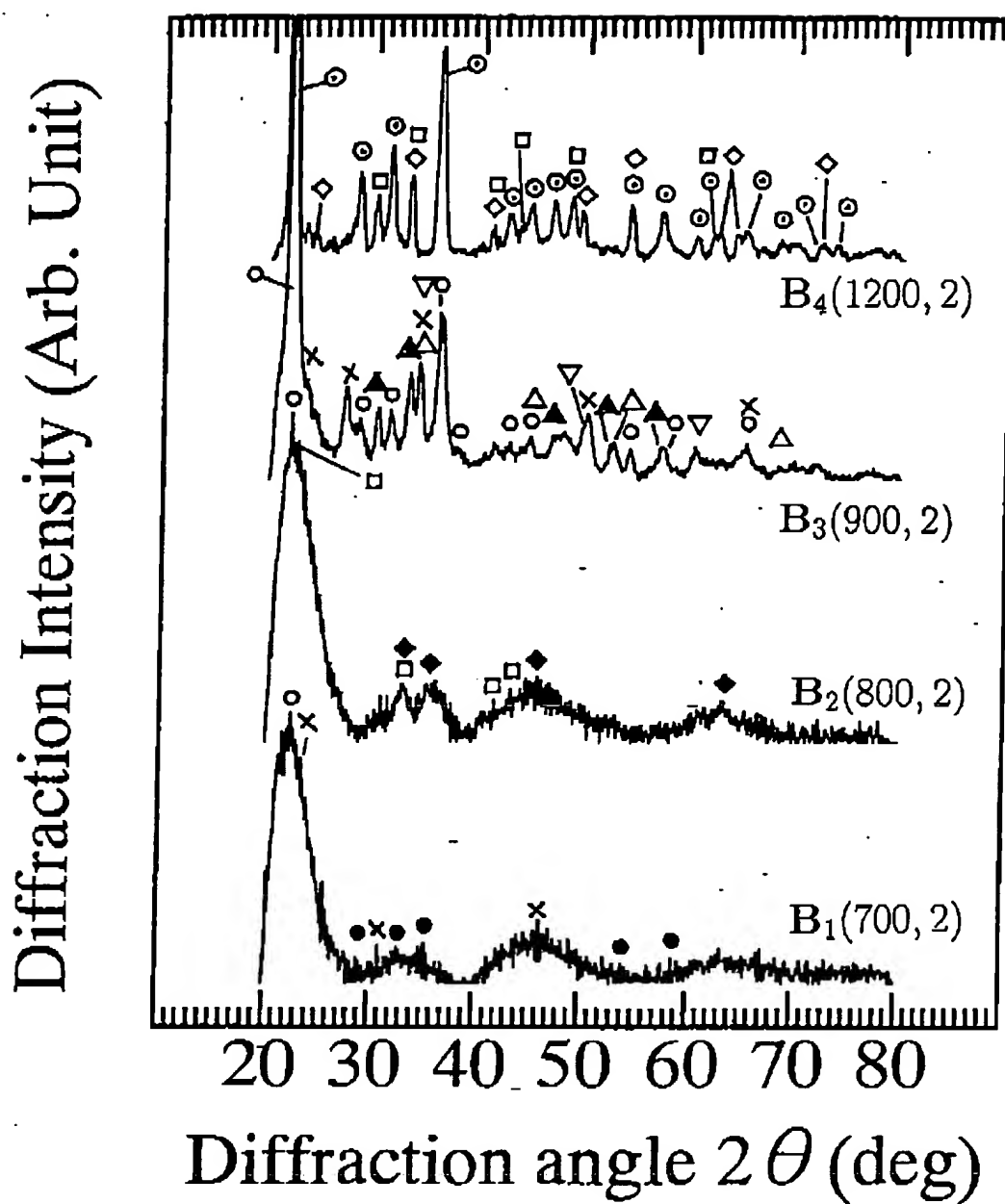
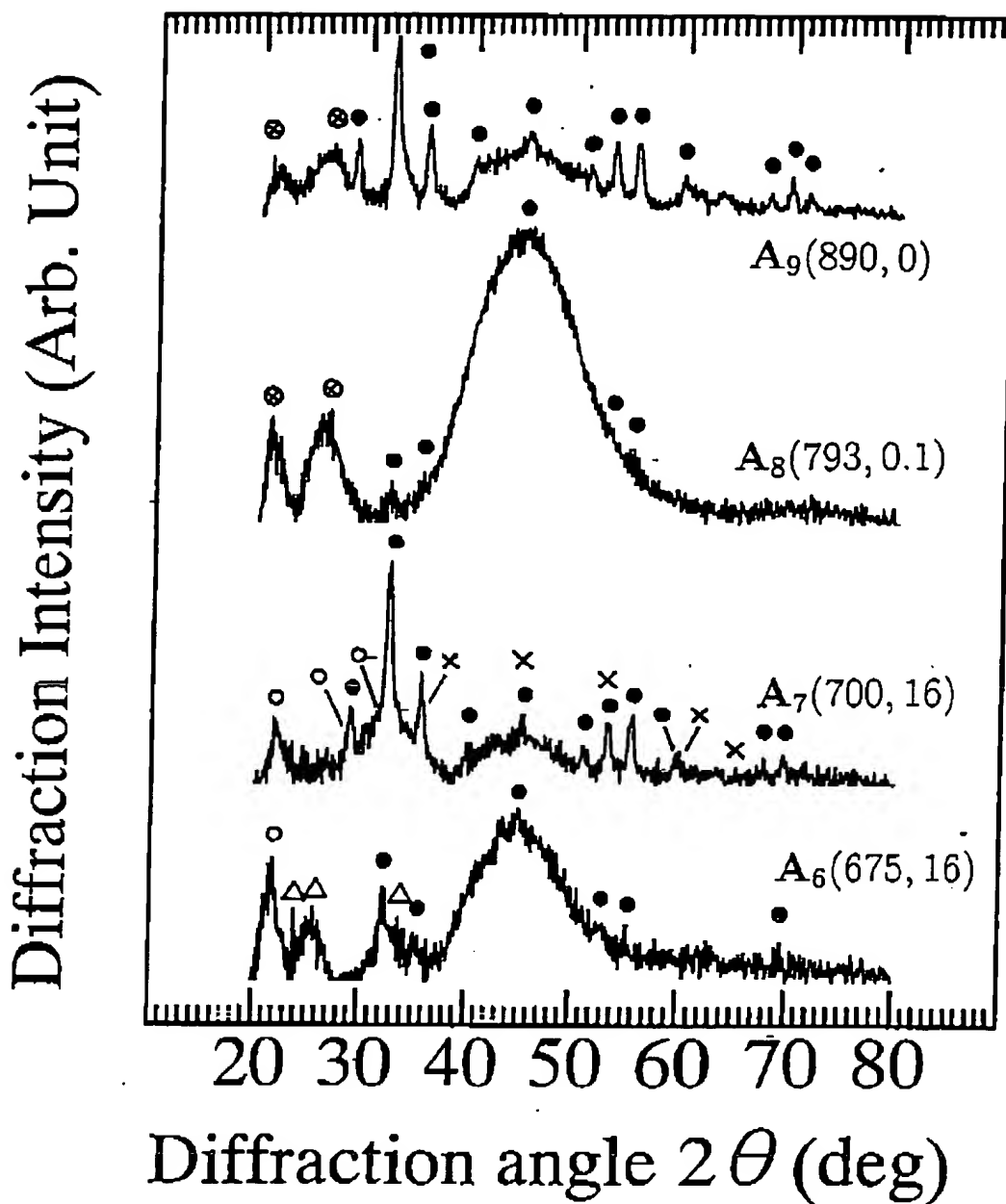
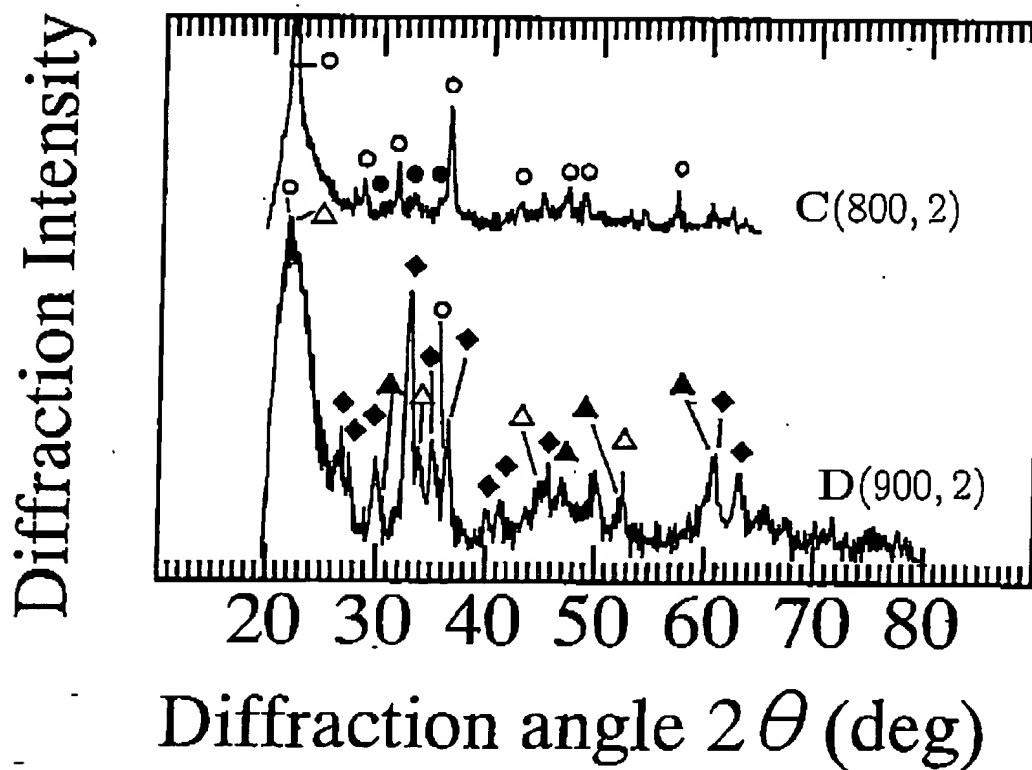


Fig. 4

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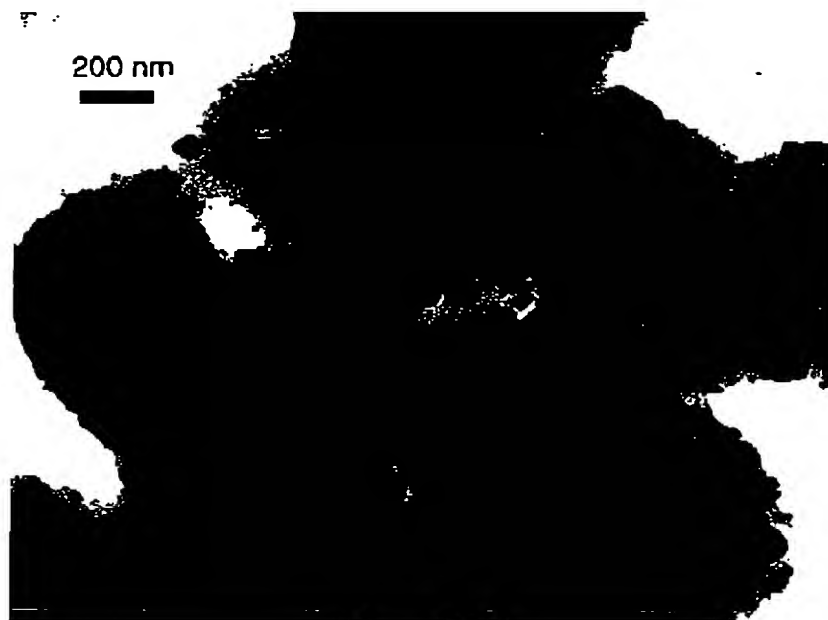
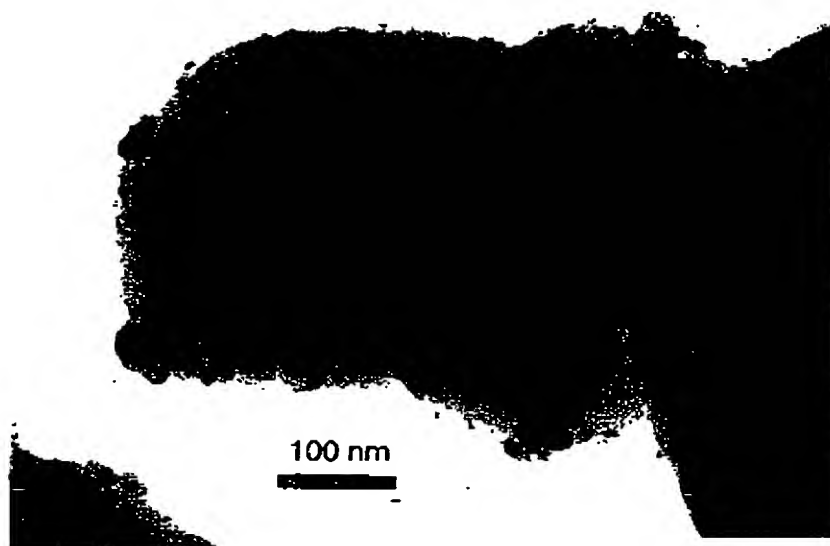


Fig 7

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